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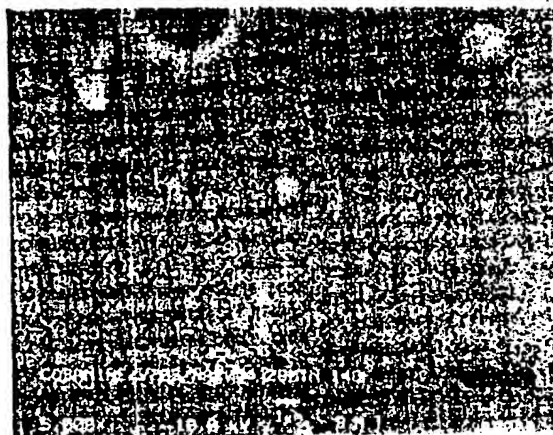
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(54) Title: IMPROVED NON-CHROMATED OXIDE COATING FOR ALUMINUM SUBSTRATES

**(57) Abstract**

An improved process that is commercially practical for forming an oxide film cobalt conversion coating exhibiting corrosion resistance and paint adhesion properties on an aluminum or aluminum alloy substrate for use in aircraft/aerospace applications (for example, an aluminum or aluminum alloy commercial airplane part), the process comprising the steps of: (a) providing an oxide film forming cobalt conversion solution comprising an aqueous reaction solution prepared by reacting the following starting materials: (1) a cobalt-II salt; (2) an ammonium salt; (3) one or more inorganic complexing agents selected from a soluble metal carboxylate, a soluble metal nitrite, or ammonia; (4) a water soluble amine; and (5) an oxidizing agent; and (b) contacting the substrate with the aqueous reaction solution for a sufficient amount of time to oxidize the surface of the substrate, whereby the oxide film cobalt conversion coating is formed, thereby imparting corrosion resistance and paint adhesion properties to the substrate. A similar commercially practical process for aluminum or aluminum alloy substrates for use in non-aircraft/aerospace applications (for example, an aluminum or aluminum alloy marine hardware part) employs the above steps, but does not include the ammonium salt in the starting materials.

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**IMPROVED NON-CHROMATED OXIDE COATING  
FOR ALUMINUM SUBSTRATES**

**1) Field Of The Invention**

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This environmental-quality invention is in the field of chemical conversion coatings formed on aluminum and aluminum alloy substrates. One aspect of the invention is an improved process of forming an oxide coating, referred to as a "cobalt conversion coating," that is chemically  
10 formed by oxidizing the surface of an aluminum or aluminum alloy substrate. The invention enhances the quality of the environment of mankind by contributing to the maintenance of air and water quality.

**2) Description Of The Related Art**

In general, chemical conversion coatings are formed chemically by  
15 causing the surface of the metal to be "converted" into a tightly adherent coating, all or part of which consists of an oxidized form of the substrate metal. Chemical conversion coatings can provide high corrosion resistance as well as strong bonding affinity with paint. The industrial application of paint to metals generally requires the use of a chemical conversion coating,  
20 particularly when the performance demands are high.

Although aluminum protects itself against corrosion by forming a natural oxide coating, the protection is not complete. In the presence of moisture and electrolytes, aluminum alloys, particularly the high-copper 2000-series aluminum alloys, such as alloy 2024-T3, corrode much more  
25 rapidly than pure aluminum.

In general, there are two types of processes for treating aluminum to form a beneficial conversion coating. The first is by anodic oxidation (anodization) in which the aluminum component is immersed in a chemical bath, such as a chromic or sulfuric acid bath, and an electric current is  
30 passed through the aluminum component and the chemical bath. The resulting conversion coating on the surface of the aluminum component offers resistance to corrosion and a bonding surface for paint.

The second type of process is by chemically producing a conversion coating, which is commonly referred to as a chemical conversion coating, by  
35 subjecting the aluminum component to a chemical solution, such as a chromic acid solution, but without using an electric current in the process.

The chemical solution may be applied by immersion application, by manual application, or by spray application. The resulting conversion coating on the surface of the aluminum component offers resistance to corrosion and a bonding surface for paint. The present invention relates to this second type of process for producing chemical conversion coatings. The chemical solution may be applied by immersion application, by various types of manual application, or by spray application.

One widely used chromic acid process for forming chemical conversion coatings on aluminum substrates is described in various embodiments in Ostrander et al. U.S. Patent 2,796,370 and Ostrander et al. U.S. Patent 2,796,371, in military process specification MIL-C-5541, and in Boeing Process Specification BAC 5719. These chromic acid chemical conversion baths contain hexavalent chromium, fluorides, and cyanides, all of which present significant environmental as well as health and safety problems. The constituents of a typical chromic acid conversion bath, such as ALODINE 1200, are as follows:  $\text{CrO}_3$  - "chromic acid" (hexavalent chromium);  $\text{NaF}$  - sodium fluoride;  $\text{KBF}_4$  - potassium tetrafluoroborate;  $\text{K}_2\text{ZrF}_6$  - potassium hexafluorozirconate;  $\text{K}_3\text{Fe}(\text{CN})_6$  - potassium ferricyanide; and,  $\text{HNO}_3$  - nitric acid (for pH control).

Many aluminum and aluminum alloy structural parts, as well as Cd plated, Zn plated, Zn-Ni plated, and steel parts, throughout the aircraft/aerospace industry are currently being treated using this chromic acid process technology. Chromic acid conversion films, as formed on aluminum and aluminum alloy substrates, meet a 168 hours corrosion resistance criterion, but they primarily serve as a surface substrate for paint adhesion. Because of their relative thinness and low coating weights (40-150 milligrams/ft<sup>2</sup>), chromic acid conversion coatings do not cause a fatigue life reduction in the aluminum and aluminum alloy structure.

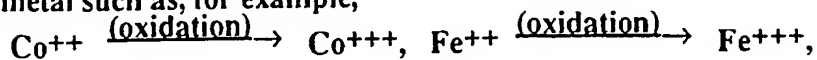
However, environmental regulations in the United States, particularly in California, and in other countries are drastically reducing the allowed levels of hexavalent chromium compounds in effluents and emissions from metal finishing processes. Accordingly, chemical conversion processes employing hexavalent chromium compounds must be replaced. The present invention, which does not employ hexavalent chromium compounds, is intended to replace the previously used chromic acid process for forming conversion coatings on aluminum and aluminum alloy substrates.

*Ito U.S. Patent 3,905,838*

Ito U.S. Patent 3,905,838 discloses a bath comprising, as the main liquid, either or both of aqueous hydrogen peroxide solution and aqueous ammonia and additionally incorporating an oxidizing agent, an inhibitor to retard liquid temperature elevation, a stabilizer for solution and, if a heavy metal is present, triethanolamine as a valency stabilizer for said heavy metal, which bath is used for treating the surface of aluminum or an alloy thereof to nonelectrolytically form a colored oxide film on the surface. In addition, Ito discloses a method of forming on the said surface, a colored oxide film by thoroughly washing the surface of the aluminum or an aluminum alloy and subsequently immersing the washed metal in the said bath.

Thus, Ito describes a bath for forming a film of aluminum oxide. The bath contains aqueous ammonia, aqueous hydrogen peroxide, an oxidizing agent (for example,  $\text{KBrO}_3$  alone or in combination with  $(\text{NH}_4)_2\text{CO}_3$ ), an inhibitor (for example,  $\text{KF}$ ,  $\text{NH}_4\text{Cl}$ , or sorbitol) which is capable of retarding the bath temperature increase and preventing the film of aluminum hydroxide from dissolution, and triethanolamine which functions as a bath stabilizer (see col. 2, line 63 - col. 3, line 9). If the bath contains a heavy metal ion, the triethanolamine functions as the valency stabilizer of the heavy metal ion (see col. 3, lines 9-11).

Ito states that when the bath is composed solely of ammonia, an oxidizing agent, hydrogen peroxide, and a heavy metal, the bath is so chemically unstable that if it is allowed to stand in its unaltered form, it will no longer function as desired after several hours of standing (see col. 4, lines 58-64). Ito states further that when such a bath (composed solely of ammonia, an oxidizing agent, hydrogen peroxide, and a heavy metal) is used to treat the aluminum alloy repeatedly, the bath readily undergoes decomposition and becomes unusable in a short period of time (see col. 4, lines 64-67). This is because, if the bath contains the salt of a heavy metal, it has its chemical composition changed by the variation of the valency of the heavy metal such as, for example,



(see col. 4, line 68 - col. 5, line 4). To preclude such change of the chemical composition of the bath, Ito incorporates in his bath the aforementioned inhibitor (for example, KF, NH<sub>4</sub>Cl, or sorbitol) for retarding the bath temperature increase and triethanolamine as a stabilizer serving to prevent possible change of the valency of the heavy metal (see col. 5, lines 4-10).

Example 4 of Ito describes preparing a bath containing 500 cc of 28% 3N NH<sub>4</sub>OH solution, 10.0g of KF, 5.0g of NH<sub>4</sub>Cl, 2.5g of NH<sub>4</sub>F•HF, 1.2g of KBrO<sub>3</sub>, 1.0g of (NH<sub>2</sub>)<sub>2</sub>CS, 0.7g of CoCl<sub>2</sub>, 0.5g of CuCl<sub>2</sub>, 0.1g of sorbitol, and 5 cc of (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (triethanolamine). CoCl<sub>2</sub> is a cobalt-II salt. As described above, Ito uses triethanolamine as a valency stabilizer serving to prevent possible change of the valency of the heavy metal. Thus, the presence of triethanolamine in Example 4 would, presumably, prevent the small amount of cobalt-II salt which is present in the solution from being oxidized and precipitating out of the solution.

15 *Tokumasu et al. U. S. Patent 4,337,097*

Tokumasu et al. U.S. Patent 4,337,097 discloses a method for making a selective absorption film for solar energy which comprises immersing aluminum or its alloy in water which contains at least two members selected from phosphate ions, fluoride ions and triethanolamine, and optionally ions of a metal selected from copper, iron, cobalt, silver and a mixture thereof thereby forming a chemical conversion film which shows a great absorptivity and a small emissivity.

### SUMMARY OF THE INVENTION

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The present invention exhibits certain improvements with respect to the processes described in the earlier related patent applications cross-referenced above: Serial No. 07/525,800 (patent application #1), Serial No. 07/621,132 (patent application #2), Serial No. 07/732,568 (patent application #3), and Serial No. 07/903,853 (patent application #4). In general, the improvements are, first, improved bath stability and consequently longer bath life, and, second, improved corrosion resistance performance exhibited by the coated aluminum or aluminum alloy substrates.

Regarding the improved bath stability, the bath of the present invention has no detectable decay rate after six months of production use. The decay rate is measured by the sludge formed in the bath. The bath of

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the present invention has no sludge in the bath after six months of production use. Furthermore, the bath performance effectiveness has not decreased in six months of production use. Another advantage is that the bath constituents are replenishable. A six-month bath life is considered a minimum for a commercially practical service life in the aircraft/aerospace industry. Thus, the present invention is a commercially practical process and a commercially practical bath.

Regarding the improved corrosion resistance performance, coated aluminum alloy substrates made by the improved process exhibit an increased level of corrosion resistance in a standard salt spray test, when tested in accordance with ASTM B117, while also exhibiting technically acceptable levels of paint adhesion when tested in accordance with the tests specified in applicable aircraft/aerospace paint specifications.

In one aspect, the invention is an improved process that is commercially practical for forming an oxide film cobalt conversion coating exhibiting corrosion resistance and paint adhesion properties on an aluminum or aluminum alloy substrate used in aircraft/aerospace applications, the process comprising the steps of:

(a) providing an oxide film forming cobalt conversion solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- (1) a cobalt-II salt;
- (2) an ammonium salt;
- (3) one or more inorganic complexing agents selected from a soluble metal carboxylate, a soluble metal nitrite, or ammonia;
- (4) a water soluble amine; and
- (5) an oxidizing agent; and

(b) contacting the substrate with the aqueous reaction solution for a sufficient amount of time to oxidize the surface of the substrate, whereby the oxide film cobalt conversion coating is formed, thereby imparting corrosion resistance and paint adhesion properties to the substrate.

In another aspect, the invention is an improved process that is commercially practical for forming an oxide film cobalt conversion coating exhibiting corrosion resistance and paint adhesion properties on a substrate used in non-aircraft/aerospace applications, where the substrate is aluminum or aluminum alloy, the process comprising the steps of:

(a) providing an oxide film forming cobalt conversion solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- (1) a cobalt-II salt;
- 5 (2) one or more inorganic complexing agents selected from the group consisting of metal carboxylates, metal nitrites, and ammonia;
- (3) a water soluble amine; and
- (4) an oxidizing agent; and

(b) contacting the substrate with the aqueous reaction solution for a  
10 sufficient amount of time to oxidize the surface of the substrate, whereby the oxide film cobalt conversion coating is formed, thereby imparting corrosion resistance and paint adhesion properties to the substrate.

In yet another aspect, the invention is a chemical conversion coating solution that is commercially practical for producing an oxide film cobalt  
15 conversion coating on a metal substrate used in aircraft/aerospace applications, the solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- (a) a cobalt-II salt;
- (b) an ammonium salt;
- 20 (c) one or more inorganic complexing agents selected from the group consisting of a soluble metal carboxylate, a soluble metal nitrite, and ammonia;
- (d) a water soluble amine; and
- (e) an oxidizing agent.

25 And in yet another aspect, the invention is a chemical conversion coating solution that is commercially practical for producing an oxide film cobalt conversion coating on a metal substrate used in non-aircraft/aerospace applications, the solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- 30 (a) a cobalt-II salt;
- (b) one or more inorganic complexing agents selected from the group consisting of a soluble metal carboxylate, a soluble metal nitrite, and ammonia;
- (c) a water soluble amine; and
- 35 (d) an oxidizing agent.



### **BRIEF DESCRIPTION OF THE DRAWINGS**

The figures are photomicrographs of images produced by a scanning electron microscope of improved cobalt conversion coatings made by the present process on aluminum alloy test panels. Thus, FIGS. 1-6 are photomicrographs (where the scanning electron microscope operated at 10 kV) of aluminum alloy 2024-T3 test panels having cobalt conversion coatings made by the invention and then given a post conversion treatment in a solution containing vanadium pentoxide and sodium tungstate (described below). FIGS. 1-6 show cobalt conversion coatings formed by a 20 minute immersion in a typical cobalt coating aqueous reaction solution at 140°F. The cobalt conversion coatings formed by the present improved process are cobalt oxide and aluminum oxide mixed structures formed by oxidizing the surface of the substrate.

FIG. 1 is a photomicrograph at 5,000X magnification of a test panel showing a cobalt conversion coating 510 of the invention. The photomicrograph is a top view of the upper surface of oxide coating 510. The top of oxide coating 510 is porous and has a sponge-like appearance as shown in FIG. 1. This test panel was immersed in the cobalt conversion coating solution for 20 minutes. The white bar is a length of 1 micron. The roundish objects are unidentified impurities on the surface of the oxide coating.

FIG. 2 is a photomicrograph at 25,000X magnification of a test panel showing a cobalt conversion coating 510 of the invention. The photomicrograph is a top view of the upper surface of oxide coating 510. The white bar is a length of 1 micron.

FIG. 3 is a photomicrograph at 50,000X magnification of a test panel showing a cobalt conversion coating 510 of the invention. The photomicrograph is a top view of the upper surface of oxide coating 510. The white bar is a length of 100 nanometers.

FIG. 4 is a photomicrograph at 5,000X magnification of a test panel showing a side view of a fractured cross section of a cobalt conversion coating 520 of the invention. The fractured cross section of the aluminum alloy substrate of the test panel is indicated by reference numeral 522. To make the photomicrographs of FIGS. 4, 5, and 6, the test panel was bent and broken off to expose a cross section of oxide coating 520. The white bar is a length of 1 micron.

FIG. 5 is a photomicrograph at 25,000X magnification of a test panel showing a side view of a fractured cross section of a cobalt conversion coating 520 of the invention. The white bar is a length of 1 micron.

FIG. 6 is a photomicrograph at 50,000X magnification of a test panel showing a side view of a fractured cross section of a cobalt conversion coating 520 of the invention. The white bar is a length of 100 nanometers.

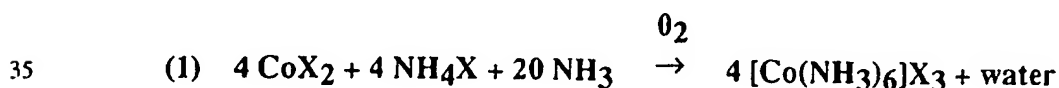
## DESCRIPTION OF THE PREFERRED EMBODIMENTS

### 10 *Historical Review And Background*

First, a considerable amount of empirical research was conducted in order to arrive at the invention described in the first patent application Serial No. 07/525,800 filed May 17, 1990, now U.S. Patent 5,298,092 issued March 29, 1994. Many multivalent compounds were investigated, used either by themselves or in combination with alkalies, acids, or fluorides. Among these compounds were vanadates, molybdates, cerates, ferrates and a variety of borates. While film deposition of compounds containing these elements on aluminum alloy substrates is achieved, none afforded any appreciable corrosion protection nor paint adhesion.

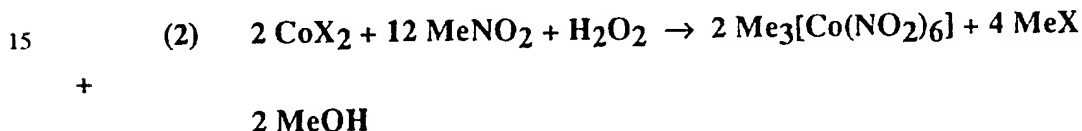
A significant increase in corrosion protection was observed, however, when aluminum substrates were immersed in aqueous solutions of simple cobalt-II ( $\text{Co}^{2+}$ ) salts heated to 180°F. This led to an investigation of a number of cobalt-II and cobalt-III ( $\text{Co}^{3+}$ ) reactions, in particular as described in application Serial No. 07/525,800 filed May 17, 1990, now U.S. Patent 5,298,092 issued March 29, 1994, and that patent is incorporated herein by reference.

In that invention, a stream of air is drawn for several hours through an aqueous solution containing a cobalt-II salt,  $\text{CoX}_2$  where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CN}, \text{SCN}, \frac{1}{3}\text{PO}_4, \frac{1}{2}\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2$ , or  $\frac{1}{2}\text{CO}_3$ , and the corresponding ammonium salt  $\text{NH}_4\text{X}$ , in the presence of ammonia to form a cobalt-III hexammine coordination complex. For example,

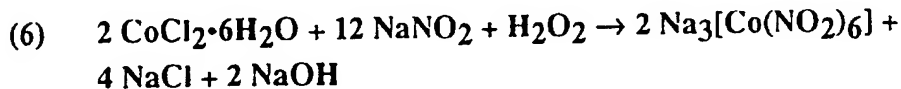
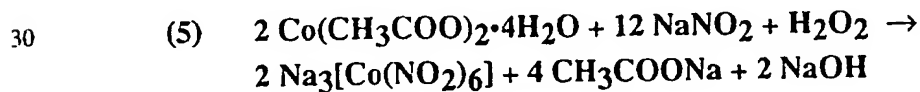
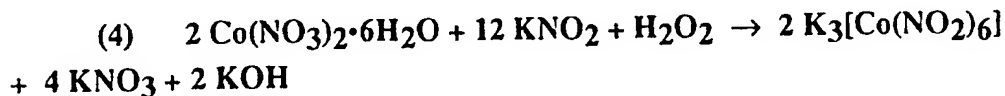
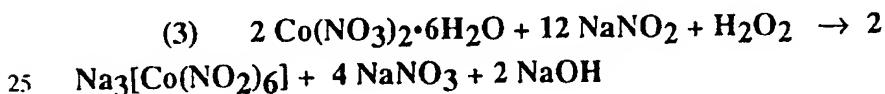


The above general reaction (1) is described in application Serial No. 07/525,800 filed May 17, 1990, now U.S. Patent 5,298,092 issued March 29, 1994. The use of ammonia was employed to make the 3-valent cobalt hexammine complex. Further research in this area has now resulted in  
5 substantial process improvements with respect to bath chemistries having a long bath life in service and an improvement in the coating performance. Salt spray corrosion resistance testing in accordance with ASTM B117 gave 336 hours (14 days) of salt spray corrosion resistance.

In the second patent application Serial No. 07/621,132 filed November  
10 30, 1990, further research revealed that when 2-valent cobalt salts are dissolved into an aqueous solution of  $\text{MeNO}_2$  (where  $\text{Me} = \text{Na}, \text{K}, \text{or Li}$ ) (alkali metal ions), in the presence of an oxidizing agent, such as  $\text{H}_2\text{O}_2$ , then 3-valent cobalt nitrite complexes are formed:

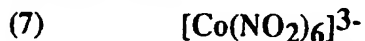


where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CN}, \text{SCN}, \frac{1}{3}\text{PO}_4, \frac{1}{2}\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2, \text{or } \frac{1}{2}\text{CO}_3$ . From  
20 an environmental standpoint, the cyanide and thiocyanate salts are not preferred. In particular, the following bath chemistries were prepared and tested:



These 3-valent cobalt nitrite complexes were found to produce brightly iridescent oxide coatings on aluminum substrates.

In the cobalt hexanitrite chemistry described above, cobalt coordination complexes are formed where the portion of the complex which includes the legend (the bracketed portion in equations (2)-(6)) is negatively charged, i.e.,

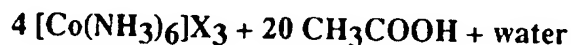
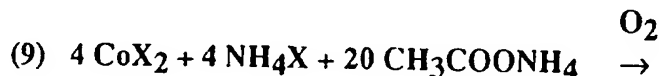


and the complete complex is



where Me corresponds to Na, K, or Li (alkali metal ions).

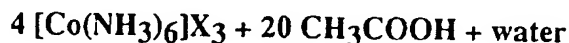
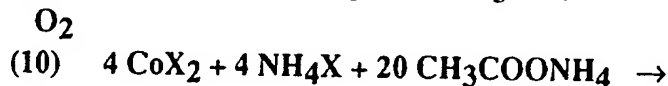
In the third patent application Serial No. 07/732,568 filed July 19, 1991, further research into cobalt-III hexammine complexes produced a significant processing advantage when ammonium hydroxide was replaced with ammonium acetate,  $\text{CH}_3\text{COONH}_4$ , i.e.,



where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CN}, \text{SCN}, \frac{1}{3}\text{PO}_4, \frac{1}{2}\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2$ , or  $\frac{1}{2}\text{CO}_3$ .

A further improvement with regard to color consistency of the oxide coating was made when the associated ammonium salt  $\text{NH}_4\text{X}$  in equation (9) was replaced with metal nitrate salts such as  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,

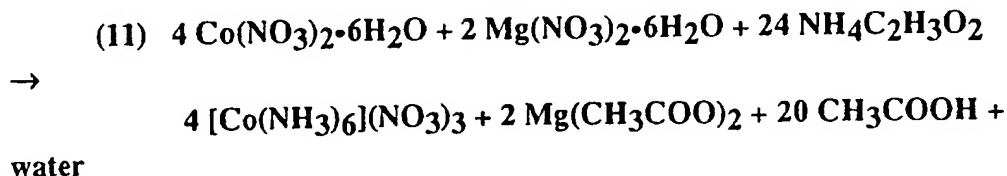
$\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , or  $\text{LiNO}_3$ , i.e.,



where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CN}, \text{SCN}, \frac{1}{3}\text{PO}_4, \frac{1}{2}\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2$ , or  $\frac{1}{2}\text{CO}_3$ .

The preferred reaction was found to involve cobalt nitrate as shown below:





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In the fourth patent application Serial No. 07/903,853 filed June 25, 1992, it was stated that the research advances described up to that point involved conversion coatings formed from the reaction of a 2-valent cobalt salt, such as cobalt nitrate with ammonium acetate to form a 3-valent cobalt complex. The resultant coatings were of high quality with regard to defined performance criteria; however, the bath lives of solutions utilizing ammonium acetate were rather short, i.e., on the order of 30 to 40 days. The desire to extend the bath life was the basis for further research.

During testing of the ammonium acetate complexed cobalt solution (Equation (11)), it was noticed that after several weeks of normal tank operation the coating weights on aluminum alloy substrates would gradually drop off and the color intensity would become lighter. In order to compensate for this, ever increasing immersion times were required. It was also noticed that a gradual solution appearance change would occur over time, from a dark brown to wine red color. Analysis finally established that a competing reaction was taking place over time, where the acetate in the complex

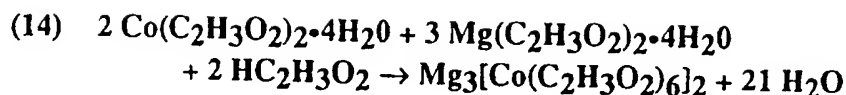
(12)  $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)]^{3-}$   
would gradually be replaced by an ammonia to form the complex

(13)  $[\text{Co}(\text{NH}_3)_6]^{3+}$

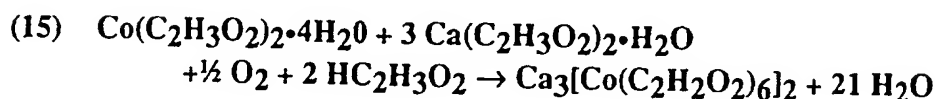
Notice the valence change in these bracketed ionic species.

In an effort to solve this problem, it was discovered, in accordance with the fourth patent application, that the substitution of a metal acetate, such as

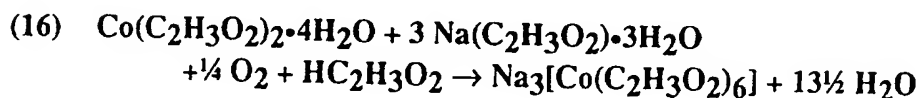
$\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$ ,  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , for the  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in equation (11) would eliminate the above competing reactions described in conjunction with complexes (12) and (13), and result in the same strong colored coatings as the original ammonium acetate solutions. Sodium acetate was the most preferred metal carboxylate. Other metal carboxylates such as zinc, lithium, potassium, and manganese acetate would work but were not preferred. The typical reactions were:



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### *Description Of The Improved Cobalt Chemical Conversion Processes*

15        The present invention exhibits improvements with respect to the processes described in the earlier related patent applications above: Serial No. 07/525,800 (patent application #1), Serial No. 07/621,132 (patent application #2), Serial No. 07/732,568 (patent application #3), and Serial No. 07/903,853 (patent application #4). The improvements are a higher bath  
20        stability and a higher corrosion resistance performance exhibited by coated aluminum alloy substrates. As a consequence of the higher bath stability, the bath life is longer.

         Regarding the improved bath stability, the bath of the present invention has no detectable decay rate after six months of production use.  
25        The decay rate is measured by sludge formed in the bath. The bath of the present invention has no sludge in the bath after six months of production use. This is a significant improvement because the baths of the four earlier patent applications have detectable decay rates, they form sludge, and they have bath lives of 2 to 3 months in production use. Furthermore, the present  
30        bath performance effectiveness has not decreased in six months of production use. Another feature of the bath is that the constituents are replenishable. A six-month bath life is considered a minimum for a commercially practical service life in the aircraft/aerospace industry (for example, for treating aircraft parts). Thus, the present invention is a commercially practical  
35        process and a commercially practical bath.

Regarding the improved corrosion resistance performance, the present coated aluminum alloy substrates exhibit an increased level 3 to 4 weeks of corrosion resistance when tested in a standard salt spray test, ASTM B117, while also exhibiting technically acceptable level of paint adhesion when tested in accordance with the tests specified in applicable paint specifications. This is a significant improvement because the best coated aluminum alloy substrates of the four earlier patent applications would exhibit 2 weeks of corrosion resistance in the salt spray test.

In the previous processes, the complexing agent was either ammonia (ammonium hydroxide  $\text{NH}_4\text{OH}$ ), or nitrites (such as sodium nitrite  $\text{NaNO}_2$ ), or acetates (such as magnesium acetate or sodium acetate). In the present improvement, the complexing agents that were previously used are partially replaced with a new complexing agent. The new complexing agent is a water soluble amine. The preferred water soluble amines for this purpose are ethylenediamine, triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA). The most preferred water soluble amine is triethanolamine (TEA).

Using a water soluble amine as an additional complexing agent, the complexing will take place with a cobalt-II salt in an aqueous solution to form certain hexacoordinated cobalt-III complexes, described below, which were not present in the baths described in the previous patent applications #1, #2, #3, and #4. For aircraft/aerospace applications (for example, for treating aircraft parts), the goal is to produce conversion coatings exhibiting maximum corrosion resistance performance while maintaining acceptable levels of paint adhesion performance. In preparing the improved cobalt conversion aqueous reaction solution or bath for such aircraft/aerospace applications, the chemical starting materials include a water soluble amine, and/or an ammonium salt (such as ammonium nitrate  $\text{NH}_4\text{NO}_3$ ), and/or an acetate complexing agent (such as sodium acetate, magnesium acetate, ammonium acetate), and/or a nitrite complexing agent (such as sodium nitrite  $\text{NaNO}_2$ ), and/or ammonia (ammonium hydroxide). Another starting material in preparing the improved cobalt conversion bath for aircraft/aerospace applications, is an oxidizer (such as hydrogen peroxide  $\text{H}_2\text{O}_2$ , potassium permanganate  $\text{KMnO}_4$ , or air oxygen). The preferred oxidizer is hydrogen peroxide  $\text{H}_2\text{O}_2$ .

For non-aircraft/aerospace applications (for example, for treating marine hardware parts), the goal is to produce conversion coatings exhibiting maximum paint adhesion performance while maintaining acceptable levels of corrosion resistance performance. In preparing the improved cobalt conversion aqueous reaction solution or bath for such non-aircraft/aerospace applications, the chemical starting materials include a water soluble amine, and/or an acetate complexing agent (such as sodium acetate, magnesium acetate, ammonium acetate), and/or a nitrite complexing agent (such as sodium nitrite  $\text{NaNO}_2$ ), and/or ammonia. Another starting material in preparing the improved cobalt conversion bath for non-aircraft/aerospace applications is an oxidizer (such as hydrogen peroxide  $\text{H}_2\text{O}_2$ , potassium permanganate  $\text{KMnO}_4$ , or air oxygen). The preferred oxidizer is hydrogen peroxide  $\text{H}_2\text{O}_2$ .

The improved cobalt conversion baths (i.e., the baths that are formed after the chemical reactions between the starting materials are substantially completed) are a complicated system possibly containing some unreacted starting materials, various chemical reaction by-products, and the reaction products (including various cobalt-III complexes).

As a comparative test, conversion coatings on aluminum alloy substrates have been formed using a bath where a water soluble amine (such as TEA) was used as the *sole* complexing agent to create cobalt-III complexes in the bath (i.e., without using any acetate, the nitrite, or the ammonia complexing agents). Conversion coatings were formed by that bath, but the conversion coatings were not technically acceptable coatings. Thus, it is a requirement of the present improved process to use a mixture of a water soluble amine as a complexing agent and at least one other complexing agent of the aforementioned inorganic complexing agents in order to form an aqueous reaction solution which includes various cobalt-III complexes, possibly some unreacted starting materials, and various chemical reaction by-products. This improved bath achieves the goal of having at least six months of service life in production use (thus making the process commercially viable) and achieves the goal of producing technically acceptable conversion coatings on aluminum alloy substrates.

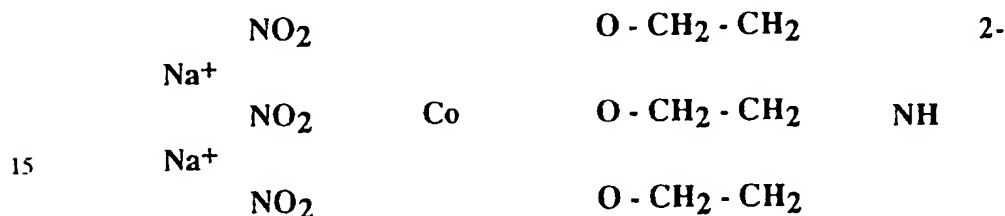
The identities of all of the chemical constituents in the improved process baths and their quantities are not known with scientific certainty because the baths are a mixture of many constituents and, at this time,



qualitative and quantitative analyses of the mixture, which require a long time and are difficult to perform, have not been completed. Furthermore, at this time the chemical mechanism by which the improved solutions perform their function is not understood, but complexing with cobalt to form cobalt-III hexacoordinated structures is believed to occur as shown below.

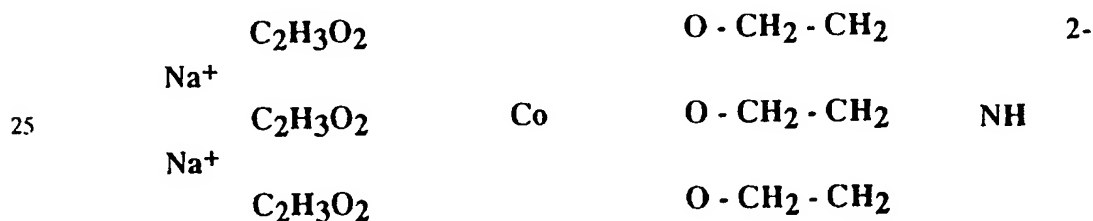
### 1. When Employing Nitrite and TEA

The primary cobalt-III complex is believed to be  $\text{Na}_2 [\text{Co}(\text{NO}_2)_3 (\text{TEA})]$ . The chemical structure of this complex is believed to be:



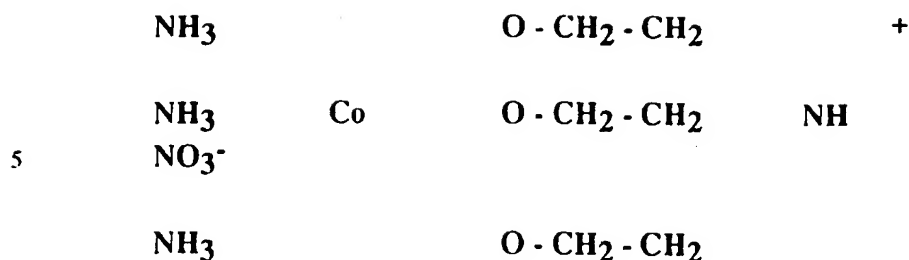
### 2. When Employing Acetate and TEA

The primary cobalt-III complex is believed to be  $\text{Na}_2 [\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_3 (\text{TEA})]$ . The chemical structure of this complex is believed to be:



### 3. When Employing Ammonia and TEA

The primary complex is believed to be  $[\text{Co}(\text{NH}_3)_3 (\text{TEA})]\text{NO}_3$ . The chemical structure of this complex is believed to be:



### *Chemical Reactant Selection (Starting Materials)*

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The most critical parameters affecting performance of the present cobalt conversion coatings with respect to paint adhesion and corrosion resistance were found to be selection of the reactants and their concentrations in solution. It was found that coating performance was affected foremost by these factors rather than bath temperature or immersion time, although temperature and immersion time do impart their effects over larger variations of these parameters.

It is known that with respect to surface treatments of aluminum, paint adhesion and corrosion resistance are divergent properties. In other words, maximizing paint adhesion usually occurs at the expense of corrosion performance and vice-versa. This surface treatment behavior was also found to exist with cobalt conversion coatings.

Regarding reactant selection, a wide variety of cobalt salts are operable for cobalt complexing. Among the cobalt-II salts that are operable in water solution are  $\text{CoX}_2$  where X is one or more selected from the group consisting of Cl, Br,  $\text{NO}_3$ , CN, SCN,  $\frac{1}{3}\text{PO}_4$ ,  $\frac{1}{2}\text{SO}_4$ ,  $\text{C}_2\text{H}_3\text{O}_2$ , or  $\frac{1}{2}\text{CO}_3$ . From an environmental standpoint, the cyanide and thiocyanate salts are not preferred. Furthermore, other cobalt-II salts may be used if they possess a minimum solubility in water.

For conversion coatings to be used in aircraft/aerospace applications, an ammonium salt is a necessary starting material. The preferred ammonium salts are ammonium nitrate and ammonium acetate. The most preferred ammonium salt is ammonium nitrate, since cobalt salts tend to have a strong reaction affinity for nitrates. For conversion coatings to be used in non-aircraft/aerospace applications, the ammonium salt is not used as a starting material.

An inorganic complexing agent is also a necessary starting material. The inorganic complexing agent may be a metal nitrite salt  $\text{MeNO}_2$ , where Me is one or more selected from the group consisting of Na, K, or Li, and/or the inorganic complexing agent may be a soluble metal carboxylate having from 1 to 5 carbon atoms, and/or the inorganic complexing agent may be ammonia. Regarding metal carboxylates, the carboxylate salts of Ca, Mg, and Na are preferred, with the Na carboxylate being most preferred while Zn, Li, K, and Mn may also be used. Metal salts of acetic acid are preferred with sodium acetate being most preferred. The limitation on using carboxylates other than the acetates is water solubility and the ability to form cobalt-III complexes.

A water soluble amine (an organic complexing agent) is necessary. The preferred water soluble amines for this purpose are ethylenediamine, triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA). The most preferred water soluble amine is triethanolamine (TEA).

A preferred chemical additive is an oxidizer, preferably hydrogen peroxide,  $\text{H}_2\text{O}_2$ . The function of the oxidizer is to oxidize the cobalt-II ions in solution to cobalt-III ions. The stream of air flowing into the tank also functions as an oxidizer, but the hydrogen peroxide increases the rate of oxidation of the cobalt-II ions in solution to cobalt-III ions and therefore is useful for commercial practice of the invention in that the solution becomes operational in a shorter period of time.

As discussed above, the improved aqueous reaction solution or conversion bath is a system wherein it is necessary to have all of the chemical constituents that result from the chemical reactions involving the starting materials. The resultant aqueous reaction solution containing many chemical constituents is needed in order to form technically acceptable oxide coatings.

To summarize, the necessary starting materials for aircraft/aerospace applications are the following:

1. A cobalt-II salt.
2. An ammonium salt.
3. An inorganic complexing agent (one or more of: metal carboxylates and/or metal nitrites and/or ammonia).
4. A water soluble amine (an organic complexing agent).
5. An oxidizing agent (such as  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , or air oxygen).

And for non-aircraft/aerospace applications, the necessary starting materials are the following (note that the ammonium salt is not used):

1. A cobalt-II salt.
- 5        2. An inorganic complexing agent (one or more of: a metal carboxylates and/or metal nitrites and/or ammonia).
3. A water soluble amine (an organic complexing agent).
4. An oxidizing agent (such as  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , or air oxygen).

10        The absence of any of the above necessary starting materials will result in a bath which will produce either no coating formation at all or coatings that do not meet corrosion resistance and paint adhesion performance requirements.

*Chemical Concentrations, pH Control, Temperature, And Immersion Time*

15        With respect to chemical concentrations, the concentration of dissolved cobalt-II salt used may be from about 0.01 mole per liter of final solution up to the saturation limit of the cobalt-II salt employed at 20°C (68°F). Preferably, the concentration of dissolved cobalt-II salt used may be from about 0.082 mole per liter of final solution to 0.10 mole per liter of final  
20        solution.

The concentration of the dissolved ammonium salt may be from about 0.03 to 2.5 moles per liter of final solution. Preferably, the concentration of dissolved ammonium salt used may be from about 0.92 mole per liter of final solution to 1.05 moles per liter of final solution.

25        The concentration of the dissolved metal nitrite salt may be from about 0.03 to 2.5 moles per liter of final solution. Preferably, the concentration of dissolved metal nitrite salt used may be from about 0.35 mole per liter of final solution up to 0.42 mole per liter of final solution.

30        The concentration of dissolved metal carboxylate may be from about 0.03 to 2.5 moles per liter of final solution. Preferably, the concentration of dissolved metal carboxylate used may be from about 0.33 mole per liter of final solution to 0.43 mole per liter of final solution.

35        The concentration of ammonium hydroxide (ammonia ) may be from about 0.03 to 0.8 moles per liter of final solution. Preferably, the concentration of dissolved ammonia used may be from about 0.20 mole per liter of final solution to 0.25 mole per liter of final solution.

The concentration of the water soluble amine may be from about 0.03 to 0.25 mole per liter of final solution. Preferably, the concentration of the water soluble amine used may be from about 0.14 mole per liter of final solution to 0.17 mole per liter of final solution.

- 5        The pH of the bath may be from about 6.0 to 7.5 with 6.8 to 7.2 being preferred. The temperature of the bath may be from about 68°F to 160°F; prolonged heating above 160°F causes gradual decomposition of the cobalt-III hexacoordinated complex. The optimum temperature is  $140 \pm 5^\circ\text{F}$ . The immersion time may be from about 3 minutes to 60 minutes with the  
10       optimum immersion time at 15 - 30 minutes.

*Examples Of The Improved Processes*

- The following examples provide specific details of the improved processes and the aqueous reaction solutions used therein. Example 1 below is a formulation for a nitrite-complexed cobalt conversion solution using  
15       TEA and nitrite mixed complexing. Example 1 represents the most preferred process for substrates used in aircraft/aerospace applications (for example, an aluminum or aluminum alloy commercial airplane part) where the goal is to produce conversion coatings exhibiting maximum corrosion resistance performance while maintaining acceptable paint adhesion  
20       performance.

**EXAMPLE 1**

COMPONENT	MAKEUP PER LITER	CONTROL PER LITER
Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	26 gm (0.089 mole)	24 - 29 gm (0.082 - 0.10 mole)
Sodium nitrite $\text{NaNO}_2$	26 gm (0.38 mole)	24 - 29 gm (0.35 - 0.42 mole)
Ammonium nitrate $\text{NH}_4\text{NO}_3$	79 gm (0.99 mole)	74 - 84 gm (0.92 - 1.05 mole)
Triethanolamine (TEA) 80 wt % minimum	26 ml (0.15 mole)	24 - 29 ml (0.14 - 0.17 mole)
Hydrogen peroxide $\text{H}_2\text{O}_2$ 30 wt %	8 ml (0.07 mole)	---
Water (deionized)	Balance	As required
Ammonium hydroxide	To adjust pH ---	As required to maintain pH
Temperature	100°F $\pm$ 5°F on makeup	140°F $\pm$ 5°F operating
pH	---	6.8 - 7.2
Immersion time	---	15 - 30 minutes

*Preferred Bath Preparation Sequence For Example 1*

5        The preferred bath preparation sequence for Example 1 above (process for aircraft/aerospace applications) is as follows:

1. A stainless steel tank (containing an inert liner) fitted with air agitation plumbing and heating coils is filled to  $\frac{3}{4}$  with deionized water at a temperature of about 100°F. Air agitation is commenced to a gentle roll.

10      The tank may be equipped with a filter unit to remove any solid impurities (dust, aluminum silt, etc.) during processing.

2. Add and dissolve the required chemicals in the following order:

- (a) Ammonium nitrate.
- (b) Sodium nitrite.
- (c) Cobalt nitrate.

(d) Triethanolamine (TEA).

3. The tank is filled to the final volume with deionized water. Air agitation of this solution is maintained. Let the solution react for 10 to 15 minutes.
- 5        4. Add the required amount of oxidizer, i.e., hydrogen peroxide  $\text{H}_2\text{O}_2$  (30 weight % preferred), and let react for one hour. The preferred amount of  $\text{H}_2\text{O}_2$  is about 8 to 10 ml of  $\text{H}_2\text{O}_2$  per liter of final solution.
5. Heat the solution to preferably about  $140^\circ\text{F}$  and let it react for an additional  $4 \pm 0.5$  hours.
- 10       6. Check the pH of the solution. If the pH is below 6.8, then add ammonium hydroxide to the solution while stirring vigorously to raise the pH to the preferred pH range of 6.8 to 7.2.
7. Optionally but preferably, a second stainless steel tank (to be used for a post conversion treatment step in accordance with Example 5 below) is prepared with air agitation plumbing and heating coils and is filled  $\frac{3}{4}$  with deionized water. This post-cobalt conversion coating step serves as a corrosion resistance promoter. The tank is left unheated while adding the required chemicals.
- 15       8. A quantity of vanadium pentoxide and a quantity of sodium tungstate are added to the second tank and dissolved. The preferred amount of vanadium pentoxide is about 2 gm (0.011 mole) per liter of final solution. The preferred amount of sodium tungstate is about 8 gm (0.024 mole) per liter of final solution. Stir as necessary to dissolve.
- 20       9. The second tank is then filled to final volume with deionized water and heated to  $140 \pm 5^\circ\text{F}$ . No further air agitation is needed.
- 25

Example 2 below is a formulation for acetate complexed cobalt conversion solutions using TEA and acetate mixed complexing. Example 2 represents a preferred process for substrates used in non-aircraft/aerospace applications (for example, an aluminum or aluminum alloy marine hardware part) where the goal is to produce conversion coatings exhibiting maximum paint adhesion performance while maintaining acceptable levels of corrosion resistance performance.

**EXAMPLE 2**

COMPONENT	MAKEUP PER LITER	CONTROL PER LITER
Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	33 gm (0.11 mole)	30 - 35 gm (0.10 - 0.12 mole)
Magnesium acetate (Preferred) $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ or Calcium acetate $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ or Sodium acetate $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$	85 gm (0.40 mole)  70 gm (0.36 mole)  54 gm (0.40 mole)	80 - 90 gm (0.37 - 0.42 mole)  65 - 75 gm (0.33 - 0.39 mole)  50 - 58 gm (0.37 - 0.43 mole)
Triethanolamine (TEA) 80 wt % minimum	26 ml (0.15 mole)	24 - 30 ml (0.14 - 0.17 mole)
Hydrogen peroxide $\text{H}_2\text{O}_2$ 30 wt %	10 ml (0.088 mole)	As required periodically to maintain coating color
Operating temperature	100°F	140 - 145°F
Bath pH	---	6.8 - 7.2
Immersion time	---	15 - 30 minutes

*Preferred Bath Preparation Sequence For Example 2*

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The preferred bath preparation sequence for Example 2 above (process for non-aircraft/aerospace applications) is similar to the above preparation sequence for Example 1, but Step 2 for Example 2 is different as follows:

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2. Add and dissolve the required chemicals in the following order:
  - (a) Magnesium acetate (or calcium acetate or sodium acetate).
  - (b) Triethanolamine (TEA).
  - (c) Cobalt nitrate.



Example 3 below is a formulation for acetate complexed cobalt conversion solutions using TEA and ammonium acetate mixed complexing.

- 5 Example 3 represents another preferred process for aircraft/aerospace applications where the goal is to produce conversion coatings exhibiting maximum corrosion resistance performance while maintaining acceptable levels of paint adhesion performance.

10 **EXAMPLE 3**

COMPONENT	MAKEUP PER LITER	CONTROL PER LITER
Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	26 gm (0.089 mole)	24 - 29 gm (0.082 - 0.10 mole)
Ammonium acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	85 gm (1.1 moles)	80 - 90 gm (1.0 - 1.2 moles)
Ammonium nitrate $\text{NH}_4\text{NO}_3$	79 gm (0.99 mole)	74 - 84 gm (0.92 - 1.05 moles)
Triethanolamine (TEA) 80 wt % minimum	26 ml (0.15 mole)	24 - 29 ml (0.14 - 0.17 mole)
Hydrogen peroxide $\text{H}_2\text{O}_2$ 30 wt %	8 ml (0.07 mole)	---
Ammonium hydroxide	To adjust pH ---	As required to maintain pH
pH	--	6.8 - 7.2
Immersion time	---	15 - 30 minutes

- 15 Example 4 below is a formulation for ammonia complexed cobalt conversion solutions using TEA and ammonia mixed complexing. Example 4 represents another preferred process for aircraft/aerospace applications where the goal is to produce conversion coatings exhibiting maximum corrosion resistance performance while maintaining acceptable levels of paint adhesion performance.

**EXAMPLE 4**

COMPONENT	MAKEUP PER LITER	CONTROL PER LITER
Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	26 gm (0.089 mole)	24 - 29 gm (0.082 - 0.10 mole)
Ammonium nitrate $\text{NH}_4\text{NO}_3$	79 gm (0.99 mole)	74 - 84 gm (0.92 - 1.05 mole)
Triethanolamine (TEA) 80 wt % minimum	26 ml (0.15 mole)	24 - 29 ml (0.14 - 0.17 mole)
Ammonium hydroxide $\text{NH}_4\text{OH}$ 30 wt % solution	26 ml (0.22 mole)	24 - 29 ml (0.20 - 0.25 mole)
Hydrogen peroxide $\text{H}_2\text{O}_2$ 30 wt %	8 ml (0.07 mole)	---
Water (deionized)	Balance	As required
Temperature	100°F $\pm$ 5°F on makeup	140°F $\pm$ 5°F operating
pH	---	6.8 - 7.2
Immersion time	---	15 - 30 minutes

*Post Conversion Treatment Solution*

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There has been a further technical improvement in the post conversion treatment that contributes to the improved corrosion resistance performance of the cobalt conversion coatings. Example 5 below is a preferred formulation for the post conversion coat treatment for TEA-nitrite complexed conversion coatings and for TEA-acetate mixed complexed conversion coatings.

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**EXAMPLE 5**

COMPONENT	MAKEUP PER LITER	CONTROL PER LITER
Vanadium Pentoxide $V_2O_5$ (preferred)	2 gm (0.011 mole)	1.5 - 3.0 gm (0.0082 - 0.016 mole)
Sodium Tungstate $Na_2WO_4 \cdot 2H_2O$	8 gm (0.024 mole)	6.5 - 10.0 gm (0.020 - 0.030 mole)
Temperature	140°F	140°F
Immersion Time	---	3 - 5 minutes
pH	---	6.8 - 7.2

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***Preferred Cobalt Conversion Coating Process Flow***

The preferred cobalt conversion coating process flow sequence may be summarized as follows:

- (1) PRECLEAN IF REQUIRED
- 10 (2) MASK AND RACK AS REQUIRED
- (3) ALKALINE CLEAN AND RINSE
- (4) DEOXIDIZE AND RINSE
- (5) FORM COBALT CONVERSION COATING
- (6) IMMERSION RINSE
- 15 (7) POST CONVERSION TREATMENT STEP
- (8) RINSE
- (9) DRY

***General Notes With Respect To The Above Process Flow***

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The cobalt conversion coating should be applied after all trimming and fabrication have been completed. Parts, where solution entrapment is possible, should not be subjected to immersion alkaline cleaning or immersion deoxidizing; manual cleaning and manual deoxidizing procedures  
25 should be used to obtain water break-free surfaces before applying cobalt

conversion treatment. A water break-free surface is a surface which maintains a continuous water film for a period of at least 30 seconds after having been sprayed or immersion rinsed in clean water at a temperature below 100°F.

- 5 Thorough rinsing and draining throughout processing is necessary as each solution should be completely removed to avoid interference with the performance of the next solution in the sequence. Parts should be processed from one step to the next without delay and without allowing the parts to dry. When it is necessary to handle wet parts, wear clean latex rubber  
10 gloves. After conversion coating, handle dry parts only with clean fabric gloves. For processing systems that require part clamping, the number and size of contact points should be kept to a minimum as necessary for adequate mechanical support.

*Precleaning*

- 15 Vapor degrease may be performed in accordance with Boeing Process Specification BAC 5408, emulsion clean in accordance with Boeing Process Specification BAC 5763, or solvent clean in accordance with Boeing Process Specification BAC 5750 if parts are greasy or oily. Parts with open faying surfaces or spot-welded joints where solution entrapment is possible should  
20 be immersed in cold water (or in hot and cold water) for 2 minutes after precleaning.

*Masking And Racking*

- Areas that do not require cobalt conversion coatings should be masked with maskants. Dissimilar metal inserts (except chromium, nickel or cobalt  
25 alloy or plating, CRES, or titanium) and non-aluminum coated plasma flame sprayed area should be masked off.

*Alkaline Cleaning*

- Alkaline clean and rinse may be performed in accordance with Boeing Process Specification BAC 5744 or BAC 5749, except for parts with open  
30 faying surfaces or spot welded joints, in which case, rinsing should be for at least 10 minutes using agitation with multiple immersions (a minimum of four times) followed by manual spray rinsing as required to prevent solution entrapment.

*Deoxidizing*

- 35 Deoxidize and rinse may be performed in accordance with Boeing Process Specification BAC 5765 except for parts where solution entrapment

is possible, which parts may be rinsed using the method described above under "Alkaline Cleaning." Castings may be deoxidized by either of the following methods:

a. Deoxidize in accordance with Boeing Process Specification BAC 5765, Solution 37, 38 or 39.

b. Dry abrasive blast castings in accordance with Boeing Process Specification BAC 5748, Type II, Class 1 and rinse.

*Other Methods Of Application*

The above formulations illustrate producing cobalt conversion coatings by immersion application. The same principles apply to producing the conversion coating by manual application and by spray application.

*The Best Modes*

For substrates for use in aircraft/aerospace applications, the best mode presently contemplated for carrying out the invention is the combination of Example 1 and Example 5. For substrates for use in non-aircraft/aerospace applications, the best mode presently contemplated for carrying out the invention is the combination of Example 2 and Example 5.

The patents, specifications, and other publications referenced above are incorporated herein by reference.

Unless indicated otherwise, in stating a numerical range for a compound or a temperature or a time or other process matter or property, such a range is intended to specifically designate and disclose the minimum and the maximum for the range and each number, including each fraction and/or decimal, between the stated minimum and maximum for the range. For example, a range of 1 to 10 discloses 1.0, 1.1, 1.2 ... 2.0, 2.1, 2.2, ... and so on, up to 10.0. Similarly, a range of 500 to 1000 discloses 500, 501, 502, ... and so on, up to 1000, including every number and fraction or decimal therewithin. "Up to x" means "x" and every number less than "x", for example, "up to 5" discloses 0.1, 0.2, 0.3, ..., and so on up to 5.0.

As will be apparent to those skilled in the art to which the invention is addressed, the present invention may be embodied in forms other than those specifically disclosed above, without departing from the spirit or essential characteristics of the invention. The particular embodiments of the invention described above and the particular details of the processes described are therefore to be considered in all respects as illustrative and not

**restrictive. The scope of the present invention is as set forth in the appended claims rather than being limited to the examples set forth in the foregoing description. Any and all equivalents are intended to be embraced by the claims.**

CLAIMS

1. A process for forming an oxide film cobalt conversion coating exhibiting corrosion resistance and paint adhesion properties on a substrate, wherein said substrate is aluminum or aluminum alloy, said process comprising the steps  
5 of:

(a) providing an oxide film forming cobalt conversion solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- (1) a cobalt-II salt;
- 10 (2) one or more inorganic complexing agents selected from the group consisting of metal carboxylates, metal nitrites, and ammonia;
- (3) a water soluble amine; and
- (4) an oxidizing agent; and
- 15 (b) contacting said substrate with said aqueous reaction solution for a sufficient amount of time to oxidize the surface of said substrate, whereby said oxide film cobalt conversion coating is formed, thereby imparting corrosion resistance and paint adhesion properties to said substrate.

20

2. The process of claim 1 wherein said water soluble amine is selected from the group consisting of ethylenediamine, triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA).

25

3. The process of claim 2 wherein said water soluble amine is triethanolamine (TEA).

4. The process of claim 1-3, wherein the step of  
30 providing an oxide film forming cobalt conversion solution comprises an aqueous reaction solution prepared by reacting the following starting materials:

- (1) a cobalt-II salt;
- (2) an ammonium salt;

(3) one or more inorganic complexing agents selected from the group consisting of a soluble metal carboxylate, a soluble metal nitrite, and ammonia;

(4) a water soluble amine; and

5 (5) an oxidizing agent.

5. The process of claim 1-4 wherein said cobalt-II salt is  $\text{CoX}_2$  where  $X = \text{Cl}, \text{Br}, \text{NO}_2, \text{CN}, \text{SCN}, 1/3\text{PO}_4, 1/2\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2$ , or  $1/2\text{CO}_3$ .

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6. The process of claim 5 wherein said cobalt-II salt is cobalt nitrate.

7. The process of claim 1-6 wherein said ammonium salt  
15 is selected from the group consisting of ammonium nitrate and ammonium acetate.

8. The process of claim 7 wherein said ammonium salt is ammonium nitrate.

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9. The process of claim 1-8 wherein said soluble metal carboxylate is selected from the group consisting of metal carboxylates having from 1 to 5 carbon atoms.

25 10. The process of claim 9 wherein said soluble metal carboxylate is selected from the group consisting of soluble metal salts of acetic acid.

30 11. The process of claim 1-10 wherein said soluble metal carboxylate is selected from the group consisting of soluble metal carboxylate salts of Ca, Mg, and Na.

12. The process of claim 11 wherein said soluble metal carboxylate is a soluble metal carboxylate salt of Na.

35

13. The process of claim 9-12 wherein said soluble metal carboxylate is sodium acetate.



14. The process of claim 1-13 wherein said soluble metal nitrite is  $\text{MeNO}_2$ , where Me is one or more selected from the group consisting of Na, K, or Li.

5        15. The process of claim 14 wherein said soluble metal nitrite is sodium nitrite.

16. The process of claim 1-15 wherein said oxidizing agent is selected from the group consisting of  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , and  
10    air oxygen.

17. The process of claim 16 wherein said oxidizing agent is hydrogen peroxide  $\text{H}_2\text{O}_2$ .

15        18. The process of claim 1-17 comprising the additional step of contacting said coated substrate with an aqueous post conversion treatment solution comprising a solution of vanadium pentoxide and sodium tungstate.

20        19. An article, such as a marine hardware part and an aircraft part produced by the process of claim 1-18.

20. A chemical conversion coating solution for producing an oxide film cobalt conversion coating on a metal  
25    substrate, said solution comprising an aqueous reaction solution prepared by reacting the following starting materials:

- (a) a cobalt-II salt;
- (b) one or more inorganic complexing agents  
30    selected from the group consisting of a soluble metal carboxylate, a soluble metal nitrite, and ammonia;
- (c) a water soluble amine; and
- (d) an oxidizing agent.

35        21. The chemical conversion coating solution of claim 20 wherein said water soluble amine is selected from the group consisting of ethylenediamine, triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA).

22. The chemical conversion coating solution of claim 21 wherein said water soluble amine is triethanolamine (TEA).

23. The chemical conversion coating solution of claim 5 20-22, wherein said solution comprises an aqueous reaction solution prepared by reacting the following starting materials:

- (a) a cobalt-II salt;
- (b) an ammonium salt;
- 10 (c) one or more inorganic complexing agents selected from the group consisting of a soluble metal carboxylate, a soluble metal nitrite, and ammonia;
- (d) a water soluble amine; and
- (e) an oxidizing agent.

15

24. The chemical conversion coating solution of claim 20-23 wherein said cobalt-II salt is  $\text{CoX}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_2, \text{CN}, \text{SCN}, 1/3\text{PO}_4, 1/2\text{SO}_4, \text{C}_2\text{H}_3\text{O}_2, \text{ or } 1/2\text{CO}_3$ .

20 25. The chemical conversion coating solution of claim 24 wherein said cobalt-II salt is cobalt nitrate.

26. The chemical conversion coating solution of claim 20-25 wherein said ammonium salt is selected from the group 25 consisting of ammonium nitrate and ammonium acetate.

27. The chemical conversion coating solution of claim 26 wherein said ammonium salt is ammonium nitrate.

30 28. The chemical conversion coating solution of claim 20-27 wherein said soluble metal carboxylate is selected from the group consisting of metal carboxylates having from 1 to 5 carbon atoms.

35 29. The chemical conversion coating solution of claim 20-28 wherein said soluble metal carboxylate is selected from the group consisting of soluble metal carboxylates having from 1 to 5 carbon atoms.

30. The chemical conversion coating solution of claim 29 wherein said soluble metal carboxylate is selected from the group consisting of soluble metal salts of acetic acid.

5        31. The chemical conversion coating solution of claim 20-30 wherein said soluble metal carboxylate is selected from the group consisting of soluble metal carboxylate salts of Ca, Mg, and Na.

10       32. The chemical conversion coating solution of claim 31 wherein said soluble metal carboxylate is a soluble metal carboxylate salt of Na.

15       33. The chemical conversion coating solution of claim 32 wherein said soluble metal carboxylate is sodium acetate.

20       34. The chemical conversion coating solution of claim 20-33 wherein said soluble metal nitrite is  $\text{MeNO}_2$ , where Me is one or more selected from the group consisting of Na, K, or Li.

35. The chemical conversion coating solution of claim 34 wherein said soluble metal nitrite is sodium nitrite.

25       36. The chemical conversion coating solution of claim 20-35 wherein said oxidizing agent is selected from the group consisting of  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , and air oxygen.

30       37. The chemical conversion coating solution of claim 36 wherein said oxidizing agent is hydrogen peroxide  $\text{H}_2\text{O}_2$ .

\*\*\*\*\*

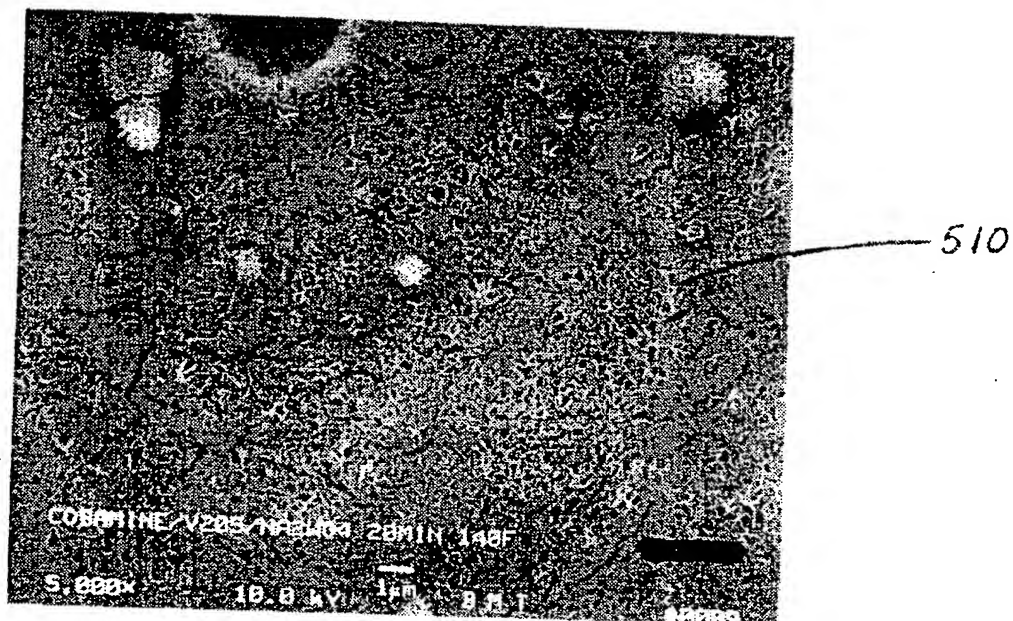


FIG. 1

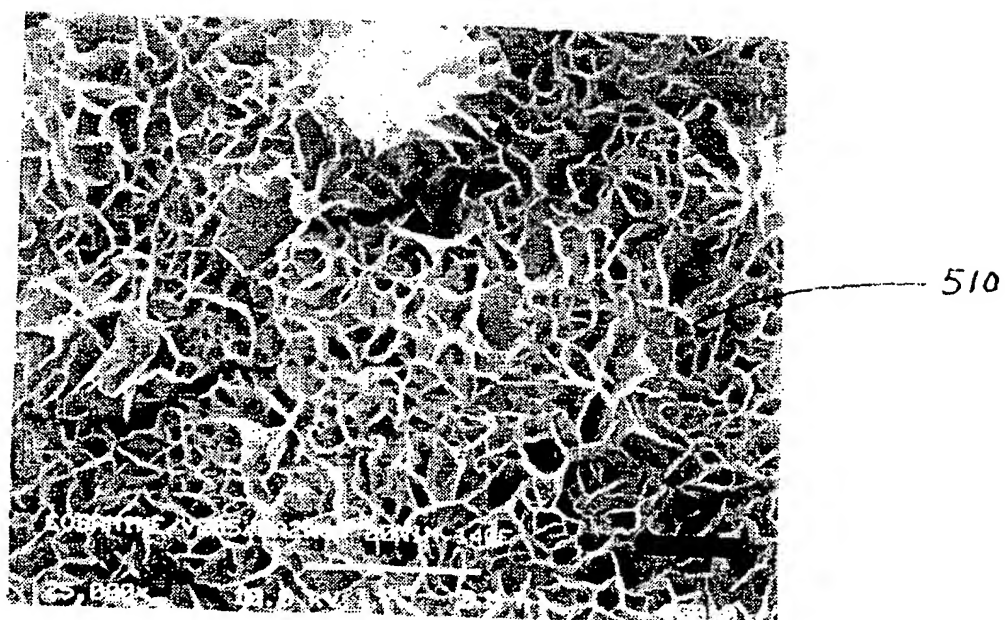


FIG. 2

SUBSTITUTE SHEET (RULE 26)

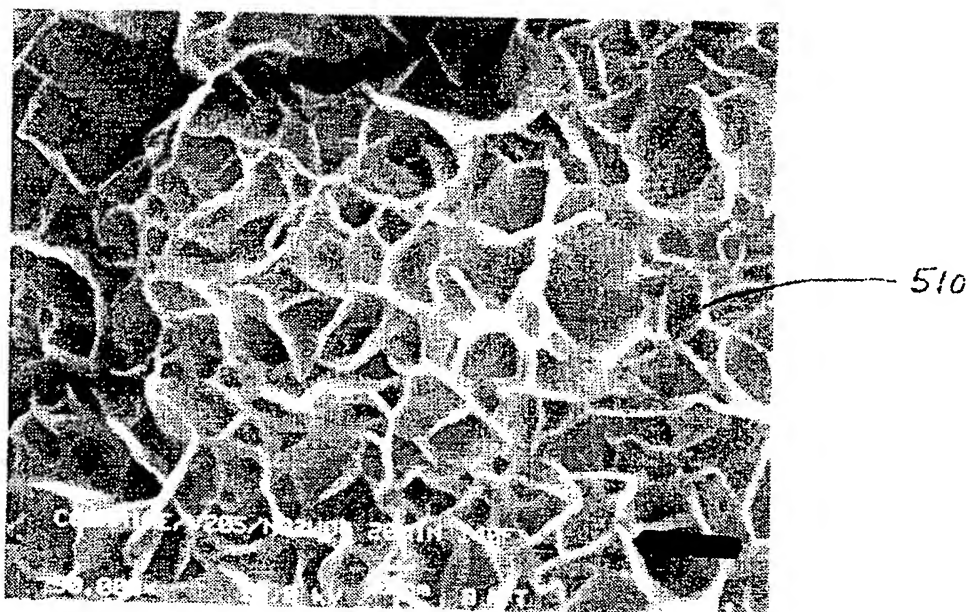


FIG. 3

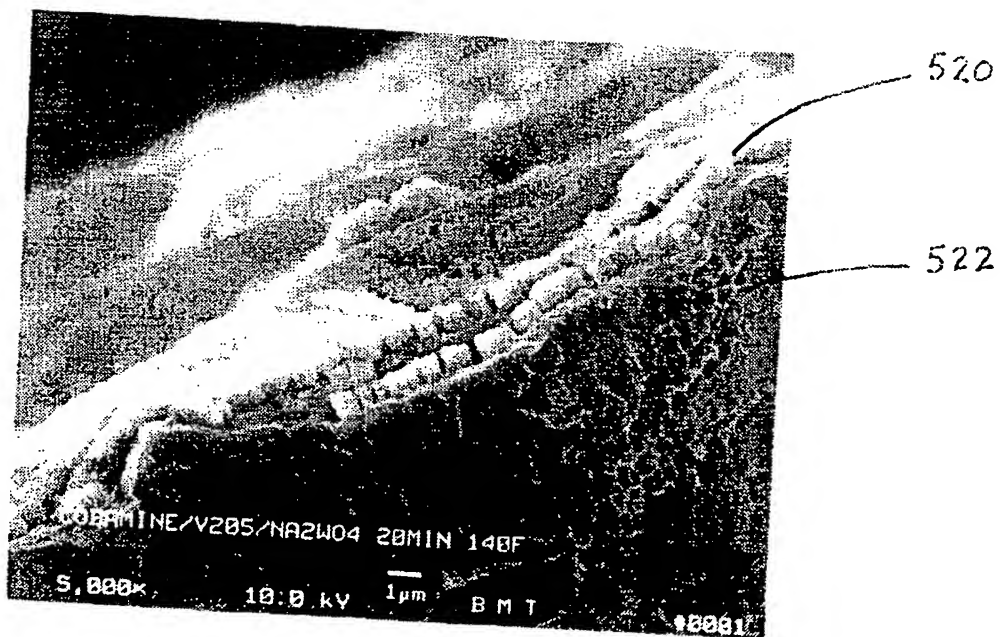


FIG. 4

SUBSTITUTE SHEET (RULE 26)

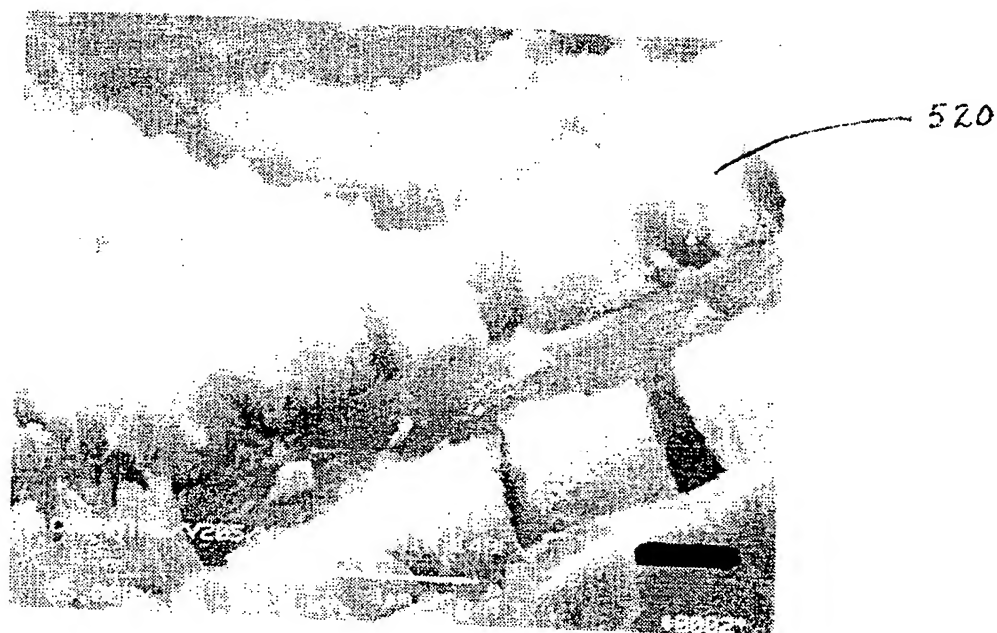


FIG. 5

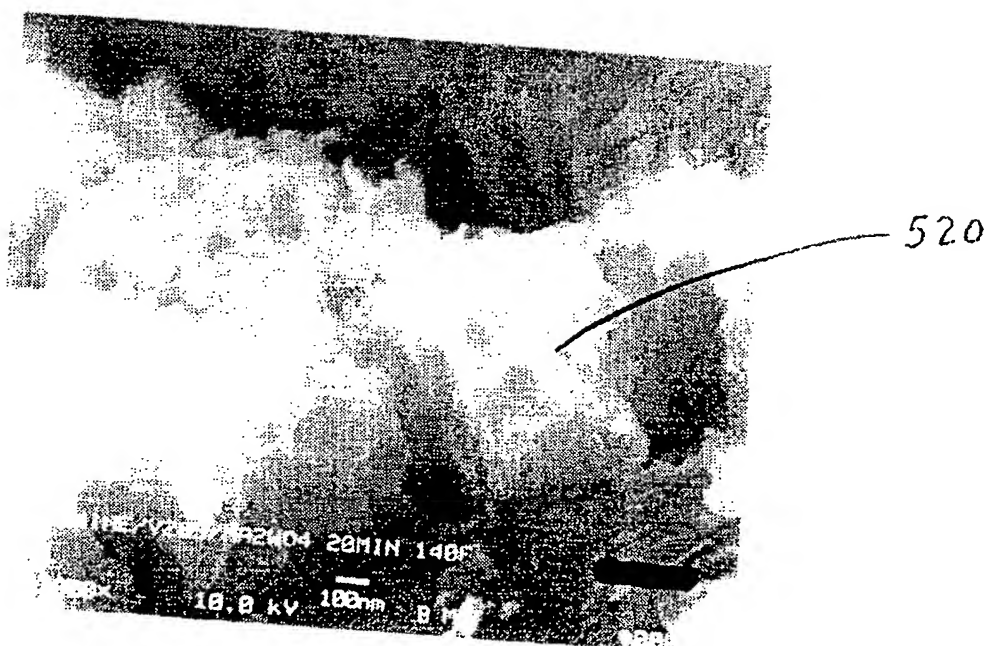


FIG. 6

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 95/03177

## A. CLASSIFICATION OF SUBJECT MATTER

C 23 C 22/56, C 23 C 22/66, C 23 C 22/68

According to International Patent Classification (IPC) or to both national classification and IPC 6

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 23 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	US, A, 5 378 293 (MATTHIAS P. SCHRIEVER) 03 January 1995 (03.01.95), abstract; claims 1-61.	1-37
A	US, A, 5 298 092 (MATTHIAS P. SCHRIEVER) 29 March 1994 (29.03.94), abstract; claims 1-51 (cited in the application).	1-37
A	EP, A, 0 523 288 (THE BOEING COMPANY) 20 January 1993 (20.01.93), abstract; claims 1-34.	1-37
A	EP, A, 0 488 430 (THE BOEING COMPANY) 03 June 1992 (03.06.92),	1-37

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search  
24 November 1995

Date of mailing of the international search report  
12. 01. 96

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# INTERNATIONAL SEARCH REPORT

-2-

International / Location No  
PCT/EP 95/03177

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>abstract; claims 1-48. --</p> <p>WO, A, 94/00 619 (THE BOEING COMPANY) 06 January 1994 (06.01.94), abstract; claims 1-82. ----</p>	1-37



zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

**ANNEX**

to the International Search  
Report to the International Patent  
Application No.

PCT/EP 95/03177 SAE 116203

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
US A	5378293	03-01-95		AU A1	88225/91	04-06-92	
				AU B2	650494	05-09-94	
				BR A	9105184	05-09-94	
				CA AA	2056168	05-09-94	
				CH AA	488844	05-09-94	
				DE AA	488844	05-09-94	
				EP AA	000000	05-09-94	
				FR AA	000000	05-09-94	
				MX A1	9105184	05-09-94	
				NZ A	9105184	05-09-94	
				US A	5411686	05-09-94	
				EP A1	450800	05-09-94	
				JP A2	7346139	05-09-94	
				US A	5346139	05-09-94	
				US A	5346139	05-09-94	
				CA AA	2056168	05-09-94	
				CH AA	488844	05-09-94	
				DE AA	488844	05-09-94	
				EP A1	450800	05-09-94	
				AU A1	450800	05-09-94	
				ON A	108097	05-09-94	
				EP A1	450800	05-09-94	
				JP T2	7346139	05-09-94	
				NO AO	945003	05-09-94	
				NO A	940061	05-09-94	
				WO A1	940061	05-09-94	
				BR A	930003	05-09-94	
				CA A	930003	05-09-94	
US A	5298092	29-03-94		EP A1	458003	07-11-91	
				JP A1	7346139	05-09-94	
				US A	5346139	05-09-94	
				US A	5346139	05-09-94	
				CA AA	2056168	05-09-94	
				CH AA	488844	05-09-94	
				AU A1	450800	05-09-94	
				EP A1	450800	05-09-94	
				FR A	5346139	05-09-94	
				CA AA	2056168	05-09-94	
				CH AA	488844	05-09-94	
				DE AA	488844	05-09-94	
				EP A2	7346139	05-09-94	
				FR A2	7346139	05-09-94	
				NZ A1	9105184	05-09-94	
				EP A1	450800	05-09-94	
				JP AO	945003	05-09-94	
				CA A1	450800	05-09-94	
				NO AO	945003	05-09-94	
				NO A	940061	05-09-94	
				BR A	930003	05-09-94	
				CA A	930003	05-09-94	
EP A1	523288	20-01-93		JP A2	504400	01-03-93	
				US A	504400	01-03-93	
				US A	504400	01-03-93	
				AU A1	504400	01-03-93	
				EP A1	504400	01-03-93	
				CA AA	2056168	05-09-94	
				CH AA	488844	05-09-94	
				DE AA	488844	05-09-94	
				EP A2	7346139	05-09-94	
				FR A2	7346139	05-09-94	
				NZ A1	9105184	05-09-94	
				EP A1	450800	05-09-94	
				JP A1	450800	05-09-94	
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